

Modeling of Hydrogen Storage Materials: A Reactive Force Field for NaH

Ojwang' J.G.O.^{*}, Rutger van Santen^{*}, Gert Jan Kramer^{*}, Adri C. T. van Duin[†] and William A. Goddard III[†]

^{*}*Schuit Institute of Catalysis, Eindhoven University of Technology, Postbus 513, 5600 MB, Den Dolech 2, Eindhoven, The Netherlands.*

[†]*Material Research Center, California Institute of Technology(Caltech), 1200 East California Boulevard Pasadena, California 91125, U.S.A.*

Abstract. Parameterization of a reactive force field for NaH is done using *ab initio* derived data. The parameterized force field(ReaxFF_{NaH}) is used to study the dynamics governing hydrogen desorption in NaH. During the abstraction process of surface molecular hydrogen charge transfer is found to be well described by the parameterized force field. To gain more insight into the mechanism governing structural transformation of NaH during thermal decomposition a heating run in a molecular dynamics simulation is done. The result shows that a clear signature of hydrogen desorption is the fall in potential energy surface during heating.

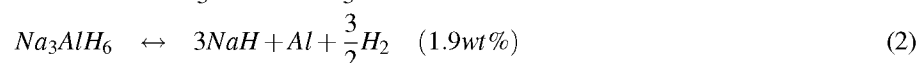
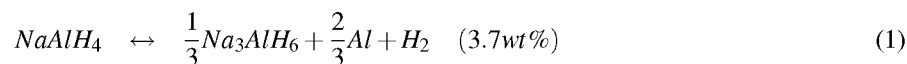
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INTRODUCTION

Bogdanovic [1] pioneered the interest in the complex metal alanates by establishing that the thermal decomposition process of NaAlH₄ could be reversed by doping with metal catalysts of which, titanium is the most thoroughly investigated. However, there are still unresolved problems in understanding of H₂ dissociation process in the system. Among these include the role of titanium (is it a dopant or a catalyst?) and long range transport mechanism of Al during the dissociation process.

Briefly, the conventional (de)sorption steps occurs as follows:



We are developing a reactive force field(ReaxFF_{NaAlH₄}) to study the structural and dynamical details of hydrogen (de)sorption processes in NaAlH₄ system. We aim to elucidate on the long range transport mechanisms of Al atoms during (de)sorption process and the dynamics governing hydrogen desorption. Towards this end we are parameterizing a force field, ReaxFF[2], to simulate large clusters containing NaH, Na₃AlH₆, NaAlH₄ and Al phases plus catalysts atoms. ReaxFF has already been shown to be able to accurately predict the dynamical and reactive processes in hydrocarbons[2], silicon/silicon oxides[3], aluminum/aluminum oxides[4] and nitramines[5].

As a run-up towards parameterizing ReaxFF_{NaAlH₄}, we have already sufficiently parameterized ReaxFF_{NaH}, which is a reactive force field for sodium and sodium hydride, to adequately describe H₂ desorption process in NaH. In this work the details of the parameterizations of ReaxFF_{NaH}, the diffusion mechanism of hydrogen atoms and hydrogen molecules in NaH and abstraction process of surface molecular H₂ in NaH cluster are examined. It will be shown that a clear signature for H₂ dissociation is the fall in potential energy surface during heating process in a molecular dynamics simulation run.

REACTIVE FORCE FIELD FOR SODIUM AND SODIUM HYDRIDE

Parametrization of ReaxFF_{NaH} has been done in line with those used to develop ReaxFF_{MgH}[6]. Initially developed for hydrocarbons[5], ReaxFF has been successfully applied to study Si/SiO₂ interfaces[3], MgH₂ systems and Al/ α -Al₂O₃ systems[4]. A key feature in ReaxFF is using the bond-order formalism that allows for bond breaking and formation as per Tersoff[7], Brenner[8] and environment dependent interatomic potential(EDIP)[9] approaches. Charge calculation are fitted using electronegativity equalization method(EEM)[10], which allows for polarizability and geometry dependent charge distribution. ReaxFF calculates non-bonded (van der Waals and Coulomb) interactions between all atoms (including 1-2 and 1-4 interactions) making it suitable for systems in which there are covalent and ionic interactions. It is this last feature, coupled with the ability to create and annihilate bonds, that makes ReaxFF attractive for modeling NaAlH₄ in which there is an interplay of both polar and covalent interactions.

The quantum values used in the fitting were obtained from VASP[11], using projector augmented[12] plane-wave method. The calculations used the generalized gradient approximation of Perdew and Wang[13, 14, 15]. The partial charges used to optimize the EEM parameters were obtained by performing a Mulliken charge distribution analysis using CRYSTAL06[16], which implements a periodic localized basis set (LCAO) approach.

The total energy expression in ReaxFF is partitioned into several contributions as follows [3]:

$$E_{\text{sys}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{NaH}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \quad (3)$$

Parameterizations of the energy expressions were done by fitting into the training set the *ab initio* derived equations of state (EoS) of pure Na and NaH condensed phases, reaction energies and bond dissociation profiles on small finite clusters. Phase transformations/crystal modifications in both Na and NaH systems during desorption process was accounted for by adding the high pressure phases of Na and NaH, in addition to the ground state phases, to the quantum calculations. In the case of Na we considered four phases: bcc-Na(8-coordinate), sc-Na(6-coordinate), fcc-Na(12-coordinate) and hcp-Na(12-coordinate). For NaH, the high pressure (CsCl-type) and NaCl-type phases were considered.

Bond dissociation

Additional tests for the reactive potential were conducted by taking into account density functional theory(DFT) values of bond dissociation profiles of small NaH clusters. Figure 1(a) shows the bond dissociation curve of NaH. ReaxFF gives an equilibrium bondlength of 1.911 Å which is in excellent agreement with DFT value of 1.929 Å. Figure 1(b) shows the NaH-NaH bond dissociation curve in which Na₂H₂ fragments into two NaH. DFT gives an equilibrium NaH-NaH bondlength of 2.076 Å while ReaxFF gives 2.108 Å. For each of these cases both DFT singlet and triplet states were considered. The bond parameters were then optimized to the lowest energy point along the dissociation profile.

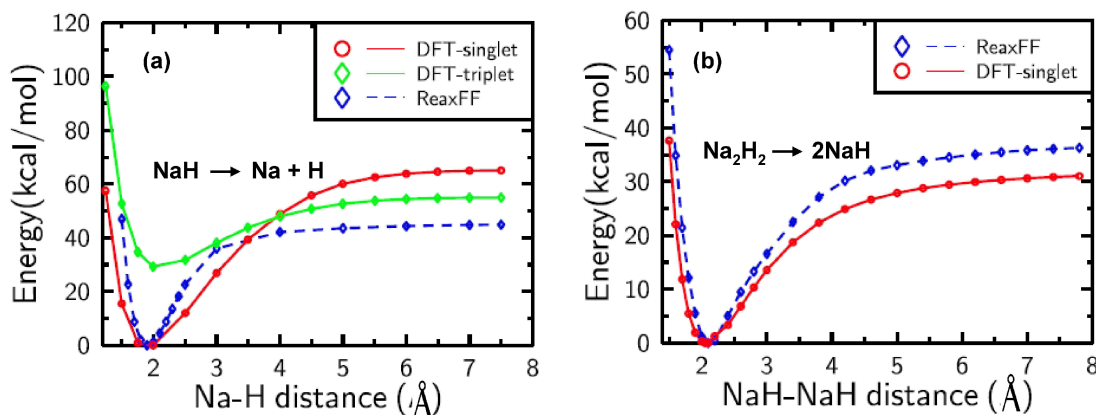


FIGURE 1. Bond dissociation curves of small clusters of NaH as calculated by DFT and ReaxFF. ReaxFF correctly captures both the short and long range behavior of the Na-H bond.

Equations of state

For both Na and NaH, the ability of ReaxFF to capture the relative phase stability was tested against a number of Na and NaH crystal modifications.

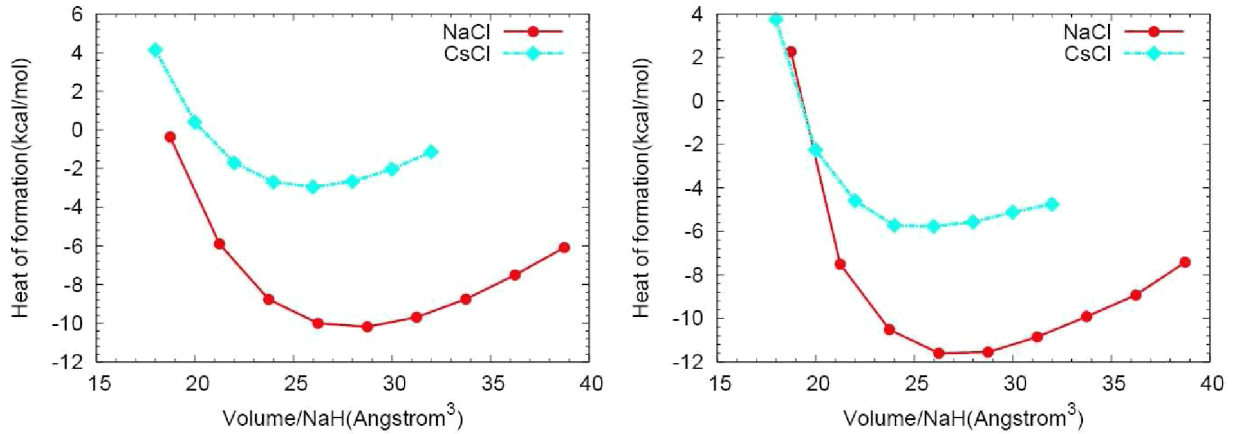


FIGURE 2. Equations of state of NaH as computed from DFT and ReaxFF respectively.

For each an every phase of Na(fcc, hcp, sc and bcc) and NaH(NaCl and CsCl types) considered in this work, the quantum energies were computed for abroad range of volume expansion and compression. The phase stabilities of ReaxFF values were compared against DFT values, Fig. 2 and table 1. There is an excellent match between DFT and ReaxFF values.

TABLE 1. Na metal and NaH phase stabilities(kcal/mol) relative to the bcc and NaCl-type phase respectively.

Na metal phase stabilities		
Phase	ΔE_{DFT}	ΔE_{ReaxFF}
HCP	0.54	0.58
FCC	0.24	0.34
SC	1.67	3.78
NaH phase stability		
CsCl-type	7.24	5.83

ABSTRACTION OF HYDROGEN

In order to get a better insight of crystal transformation during the desorption of hydrogen, we simulated successive abstraction of surface molecular hydrogen from $Na_{48}H_{48}$ cluster. The abstraction process is given by:



where $n = 46$ to 0 .

In the abstraction process, clusters were first minimized to find the nearest metastable conformation and then equilibrated at 300 K for 50000 steps(timestep was set at 0.25 fs). The clusters were then annealed to 0 K before abstraction of H_2 molecule as in the starting configuration of each simulation was the last configuration of the previous simulation's annealed run less two H atoms. This was done iteratively until all the H_2 atoms were removed.

There are two stages shown in Fig. 3(a), which shows that there is a non-linear trend in particle stability with respect to molecular hydrogen abstraction. During the abstraction process, the surface hydrogen atoms are removed first. As a result of this, some of the bulk Na atoms comes to the surface to replace the depleted hydrogen atoms. In the starting

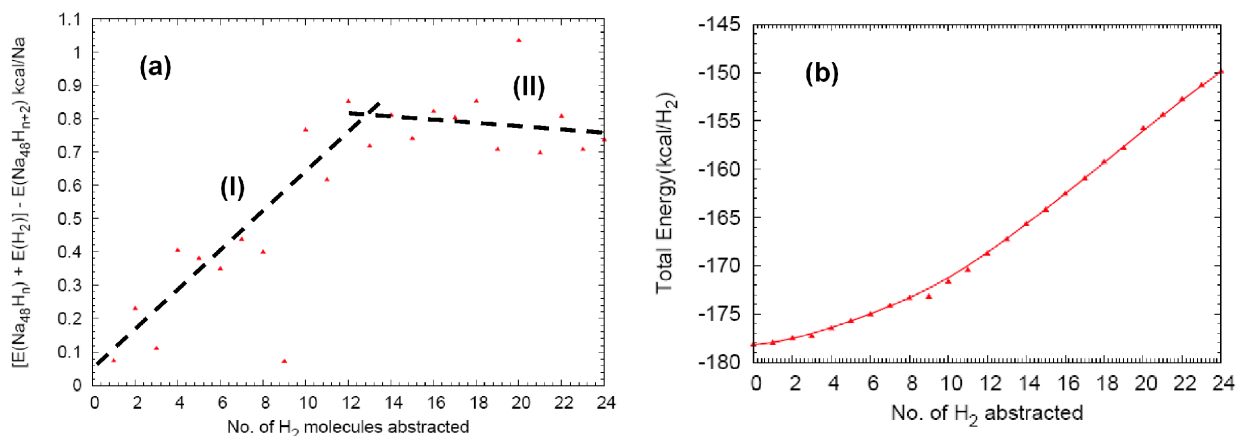


FIGURE 3. (a) Abstraction energy, $\Delta E = [E(Na_{48}H_n) + E(H_2)] - E(Na_{48}H_{n+2})$ kcal/Na and (b) Total energy as a function of number of H_2 molecules abstracted from the system.

structure, the surface hydrogen atoms mostly occupy the less stable two fold (bridge) sites. However, as more and more surface molecular hydrogen are abstracted the remaining hydrogen atoms adopts a subsurface conformation and they occupy three and four fold sites. With increasing depletion of hydrogen atoms, the sodium atoms in the bulk replaces the depleted hydrogen atoms. Therefore, the hydrogen atoms are more strongly bound in the system. This explains the trend in part (I) of Fig. 3. What is interesting about Fig. 3(a) is the change in the graph, (II), after slightly more than a half of the hydrogen atoms have been abstracted from the system. The reason for this change is that metallization dominates over ionization. We can think of this stage as a situation whereby hydrogen atoms are dissolved in Na metal matrix, with the metal retaining its metallic nature. Figure 3(b) shows the total energy as a function of the number of H_2 molecules. The graph shows that with increasing abstraction of H_2 molecules the system becomes less stable. The structure at the end, $48Na + \frac{48}{2}H_2$, is less stable than the starting structure, $Na_{48}H_{48}$. This is expected since the heat of formation of NaH is negative indicating that it is more stable with respect to its constituent elements. The scattering in Fig. 3(a) is related to the rearrangement and cluster fragmentation during the abstraction process. In other words, abstraction destabilizes the system.

MOLECULAR DYNAMICS SIMULATION

One of the goals of ReaxFF_{NaH} is to investigate the thermally induced desorption of hydrogen molecules in NaH. To do this, we performed a NVT simulation on a small cluster of NaH($Na_{24}H_{24}$) by heating it from 300 K to 1800 K using Berendsen thermostat[17]. Velocity Verlet algorithm with a timestep of 0.25fs was used in all simulation runs. The heating rate was set at 0.025 K/ps(2.5×10^{10} K/s). The cluster was first minimized to find the nearest metastable state and then equilibrated at 300 K for 5×10^4 steps. The temperature of the system was then increased linearly from 300 K to 1800 K as

$$T(t) = T_{300K} + \lambda t \quad (5)$$

where λ is the heating rate.

Figure 4 shows the time evolution of the potential energy landscape(PES) during a heating simulation of NaH from 300 K to 1800 K. We notice that at 10.275 ps and 15.75 ps there are drops in PES which, is attributed to the release of H_2 . Thus the conformation immediately before the release of H_2 was enthalpically unstable with respect to that at the release of H_2 . This instability is tied to break up of chemical bond, whereby the two hydrogen atoms break away from NaH cluster and in the process form hydrogen molecule. When a bond breaks, its chemical potential energy is converted into kinetic energy leading to temperature rise. This temperature rise leads to increased atomic motion. The desorbed hydrogen molecule uses this energy to move away from the cluster surface.

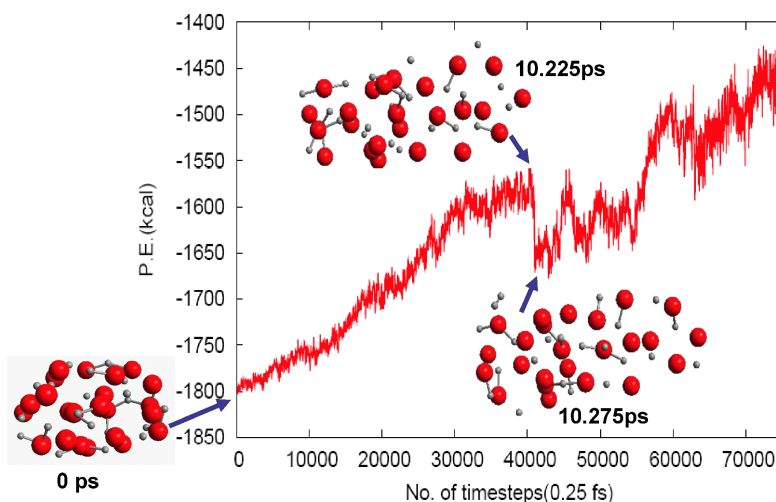


FIGURE 4. Conformational potential energy landscape during heating of NaH cluster from 300K to 1800 K.

CONCLUSION

We have parameterized a reactive force field, ReaxFF_{NaH}, for Na and NaH systems by using DFT derived values for bond dissociation profiles, charge distribution, reaction energy data for small clusters and equations of state for Na and NaH condensed phases. ReaxFF_{NaH} has been extensively used to sample the phase space and understand the dynamics governing hydrogen desorption during the thermal decomposition of NaH. During the heating run in molecular dynamics simulation, the signature of hydrogen desorption was a fall in the potential energy surface. This sets us on a firm footing towards parameterizing a force field for NaAlH₄.

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REFERENCES

1. B. Bogdanovic and M. Schwickardi. *J. Alloys and Compds*, 253, 1997.
2. A. Strachan, A. C. van Duin, D. Chakraborty, S. Dasgupta, and W. A. Goddard. *Phys. Rev. Lett.*, 91(9):098301–+, 2003.
3. A. C. T. van Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu, and W. Goddard III. *J. Phys. Chem. A*, 107:3803, 2003.
4. Q. Zhang, T. Çağın, A. C. T. van Duin, W. A. Goddard, Y. Qi, and L. G. Hector. *Phys. Rev. B*, 69(4):045423–+, 2004.
5. A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. Goddard III. *J. Phys. Chem. A*, 105:9396, 2001.
6. Sam Cheung, Wei-Qiao Deng, A. C. T. van Duin, and W. Goddard III. *J. Phys. Chem. A*, 109:851–859, 2005.
7. J. Tersoff. *Phys. Rev.*, 61:2879, 1988.
8. D. W. Brenner. *Phys. Rev. B*, 42:9458–9471, 1990.
9. M. Z. Bazant and E. Kaxiras. *Phys. Rev. Lett.*, 77:4370–4373, 1996.
10. W. J. Mortier, S. K. Ghosh, and S. J. Shankar. *J. Am. Chem. Soc.*, 120:2641, 1998.
11. G. Kresse and J. Furthmüller. *Phys. Rev. B*, 54:11169–11186, 1996.
12. P. E. Blöchl. *Phys. Rev. B*, 50:17953–17979, 1994.
13. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais. *Phys. Rev. B*, 46:6671–6687, 1992.
14. J. P. Perdew, K. Burke, and Y. Wang. *Phys. Rev. B*, 54:16533–16539, 1996.
15. J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865–3868, 1996.
16. R. Dovesi, M. Causa', R. Orlando, C. Roetti, and V. R. Saunders. *J. Chem. Phys.*, 92:7402–7411, 1990.
17. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. Dinola, and J. R. Haak. *J. Chem. Phys.*, 81:3684–3690, 1984.